A Possible Relationship Between the Composition Dependence of Ag Photodissolution and Fragility in Amorphous Ge-S

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Abstract By analyzing the composition dependence of the total amount of Ag photodissolved into amorphous Ge_xS_{1-x} and the fragility of Ge_xS_{1-x}, it is found that at the composition where the amount of Ag photodissolved exhibits a maximum, the fragility shows a minimum, that is, there is an inverse correlation between these two quantities. The possible origin of the correlation found has been discussed by using the constraint theory and the model of fragility proposed by one of the authors.

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1. Introduction

Glassy chalcogenide semiconductors show a wide variety of light induced phenomena such as photodarkening, photobleaching, photo-polymerization, photodoping, etc.[1-4]. In the photodoping phenomenon, illumination induces the dissolution of metals such as Ag into glassy chalcogenide semiconductors. Despite the extensive studies [1-5] performed after its discovery [6], theory concerning the microscopic mechanism of photodoping has not yet received general acceptance.

In order to gain further understanding on the photodoping phenomena, studies concerning the composition dependence of materials properties will be valuable. Furthermore, studying the relationship between different quantities may provide new insights to understand the complex phenomenon of photodoping.

The composition dependence of photodoping rate of Ag in As_xS_{1-x} glasses exhibit a maximum in the composition range $0.2-x-0.4$.[7,8]. Such a behavior has been discussed in the light of thermodynamic model proposed by Owen et al. [9]. Although the application of thermodynamics concepts to non-equilibrium glassy systems remains as a fundamental problem, the thermodynamic approach seems very successful. Concerning this point, it is argued that the free energy can be defined within the experimental timescales. Regarding the composition dependence of photodoping rate of Ag in As_xS_{1-x} glasses, the possible role of concentration fluctuations and excess volume has been also pointed out [10]. In the present report, the possible correlation between the total amount of photodissolved Ag into amorphous Ge_xS_{1-x} and the fragility of Ge_xS_{1-x} is investigated.

2. Composition Dependence of Photodissolution and Fragility

2.1 Photodissolution

The composition dependence of the total amount of Ag photodissolution in Ge_xS_{1-x} system has been measured by Kawaguchi and Maruno [11]. There it has been found that the total amount of Ag photodissolved exhibit a maximum value at the stoichiometric composition GeS_2. Such a result has been interpreted in terms of the glass forming ability of Ag-Ge-S. In Fig.1, the normalized value of the total amount of Ag photodissolved, Y, is shown.

The constraint counting model introduced by Phillips [12] and extended by others [13,14] provides a useful scale to study the composition dependence of chalcogenide glassy systems. According to this model, the average coordination number, $< r >$, in the

network of Ge_xS_{1-x} system is written as

$$< r >= 4x + 2(1-x) = 2x + 2 \quad . \tag{1}$$

Several studies show that many glass properties have two extrema when they are investigated as a function of $< r >$ [15]. The first extrema occurring around $< r >= 2.4$ arises from topological considerations, and it is called physical threshold or floppy-rigid transition. The second extrema occurring around $< r >= 2.67$ is called chemical threshold, and it has been understood on the basis of chemically ordered covalent network model and network dimensionality [13].

In the upper horizontal axis of Fig.1, the average coordination number is used. It is interesting to note that Y exhibit a maximum at the composition corresponding near to $< r >= 2.67$. It indicates that the Ge-S system can incorporate the largest amount of Ag when the network structure of Ge-S changes from 2-dimentional to 3-dimensional.

2.2 Fragility

The concept of fragility introduced by Angell [16] has been widely used to study the properties of supercooled liquids and the glass transition. By plotting the logarithm of the viscosity η as a function of the reduced inverse temperature T_g / T, where T_g is the glass transition temperature, curves with different degrees of non-Arrhenius behavior may be systematized. The degree of deviation from the Arrhenius behavior is called fragility and is defined as

$$F = \frac{R}{T_g}\left(\frac{\partial \ln \eta}{\partial (1/T)}\right)_{T_g} \quad , \tag{2}$$

where R is the gas constant. For highly polymerized network glass formers such as SiO_2, nearly straight lines in $\ln \eta$ Vs T_g / T plot are observed. These types of materials exhibit small values of fragility and are called strong systems. On the other hand, for systems with non-directional interatomic or intermolecular bonds such as ionic and organic liquids, strong deviations from the Arrhenius behavior are observed. Those types of materials exhibit large value of fragility and are called fragile systems. Therefore, the fragility contains information on how sensitive is the mesoscopic structures of the liquid to the variation of the temperature. Related with this observation, a model for the fragility has been proposed recently by one of the authors [17]. According to the model, the fragility is determined by the relaxation of structural units that form the melt, and is described in terms of the bond strength, E_0,

coordination number, Z_0, and their fluctuations, ΔE and ΔZ of the structural units. More explicitly, the model describes the temperature dependence of the viscosity as,

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{Cx + Cx^2\left\{\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right]\frac{(1-B)}{C} - 1\right\}}{1 - Bx^2} - \frac{1}{2}\ln(1 - Bx^2) \quad , \tag{3}$$

where

$$B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_g^2} \quad , \qquad C = \frac{E_0 Z_0}{RT_g} \quad , \qquad \text{and} \quad x = \frac{T_g}{T} \quad .$$

From Eqs. 2 and 3, the following expression for the fragility is obtained,

$$F = \frac{B - C + 2\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right]}{1-B} R \quad . \tag{4}$$

In the above expressions, η_0 and η_{Tg} are the viscosities at the high temperature limit and at the glass transition temperature, respectively. For these quantities, the usual values η_0=10^{-5} Pa·s and η_{Tg}=10^{12} Pa·s are adopted [16]. It has been shown that strong systems are characterized by large values of total bond strength, C, and small values of their fluctuations, B. On the other hand, fragile systems are characterized by small values of C and large values of B [17].

The glass system may be considered as a frozen liquid. Therefore, the characteristics of the supercooled liquid are expected to be dragged into the glassy state. In view of the above mentioned picture for the fragility, it will be interesting to investigate if there is any correlation between the degrees of fragility and the phenomena of photodoping.

The viscosity of the system Ge_xS_{1-x} has been measured by Málek and Shánělová [18]. Their data have been fitted by using the theoretical expression given by Eq. 3. The result of the fitting is shown in Fig.2 for the compositions x = 0.33 and x =0.42. We can see that Eq. 3 describes quite well the experimental data. The fitting for other concentrations, x =0.30, 0.38, 0.40 and 0.44 are also satisfactory. The values of the fragility obtained from the fitting of experimental data are shown in Fig.1. We can see that the fragility of Ge_xS_{1-x} in the concentration range of $0.30 < x < 0.45$ increases with the concentration of Ge.

It has been shown that the steepness index and the ΔC_p of Ge_xS_{1-x} system exhibit

small values and small composition dependences in the range that extends approximately from x=0.33 to x=38 [18]. The steepness index is another parameter of fragility with a meaning similar to Eq. 2 and ΔC_p is the excess heat capacity defined as the difference between heat capacity of glasses and liquid states. It is known that systems which have structures rapidly degrading with temperature are characterized by large ΔC_p values, while those which have temperature resistant structure exhibit a small ΔC_p. Therefore, a positive correlation exists between ΔC_p and the fragility. Based on these observations, we can say that for 0.33< x <0.45, Y increases as the value of the fragility decreases as shown in Fig. 1. However, unfortunately, due to the limited range in the measured composition dependence of the viscosity, a clear correlation with the composition dependence of Y can not be confirmed. In order to overcome this situation, result from other measurement is invoked below.

In glassy materials, the low frequency Raman scattering arises from two kinds of contributions [19] The first is the quasielastic scattering, which is usually ascribed to some kind of relaxation motion. The second is the so-called boson peak, which is ascribed to vibration motion. It has been recognized that the Raman spectra in disordered systems exhibit a minimum at certain frequency, which is between those frequencies characterizing the relaxation and vibration modes. Sokolov et al. [19] showed that the ratios of the intensities at the minimum to that at the boson peak maximum, $I_{\min} / I_{\max}$, correlates with the degree of fragility.

In Fig.1, the composition dependence of $I_{\min} / I_{\max}$ for the Ge_xS_{1-x} system reported by Wang et al. [20] is shown. We can see that it exhibits a maximum and a minimum value around $< r >= 2.4$ and $< r >= 2.67$, respectively. The behavior of $I_{\min} / I_{\max}$ around $< r >= 2.4$ is due to the floppy-rigid network transformation. Note that the behavior of $I_{\min} / I_{\max}$ parallels the behavior of the fragility determined by viscosity measurements in the composition range 0.33> x >0.45, where the data is available. For the composition x =0.30 a deviation seems to exist. However, by taking into consideration the behavior of the steepness index and ΔC_p mentioned above, further studies on composition dependence of viscosity for x <0.3 will be necessary in order to judge if the deviation at x =0.30 is true or not.

Comparing the behaviors of Y and $I_{\min} / I_{\max}$, we note that there is an inverse correlation in the composition range 0.20< x <0.45. The result shown in Fig.1 can be

explained as follows. When the average coordination number approaches $< r >= 2.67$, the structural units that form the system become more ordered. Here, the dominant structural unit is a tetrahedral $Ge(S_{1/2})_4$ unit. Since the total bond strength is expected to take a maximum value at this stoichiometric composition, the fragility takes a minimum value. In other words, at this composition the parameter C takes a large value. As the composition of Ge deviates from x=0.33, the structural disorder increases accompanied by the increase in the number of some kind of defects such as homopolar Ge-Ge bonds for x>0.33. Such a local network disorder is related with the fluctuation in the structural units and their connectivity, which lead to the increase of the fragility. According to the model of fragility presented above, these kind of behavior is described by the parameter B. The chemical ordering occurring at the composition corresponding to $< r >= 2.67$, imply that the stability of the system increases at this composition. From the ion transport point of view, it has been suggested that the presence of certain degree of connectivity or rigidity in the bonding between atoms is favorable for the occurrence of a large ionic conductivity [21]. It arises because the connectivity of the bonds originates the collective motion of the ions [22]. Therefore, it is probable that the stability of Ge_xS_{1-x} at x=0.33 are related with the large value of Y at this composition. The mechanism of Ag photodissolution may occur by the photoexcitation of lone pair electrons of the chalcogen atoms as suggested earlier [5]. It must be also pointed out that the molar volume of Ge_xS_{1-x} exhibit a maximum at x=0.33 [23]. This observation is in harmony with the suggestion that the photodoping rate maxima observed in As_xS_{1-x} glasses at $0.2< x <0.4$ is related with the excess volume in the system [10].

§3. Conclusion

The correlation between the total amount of photodissolved Ag into amorphous Ge_xS_{1-x} and the fragility of Ge_xS_{1-x} has been investigated. It is found that, at the composition where the total amount of photodissolved Ag exhibit a maximum, the fragility exhibit a minimum. As far as he authors are informed, this is the first work that attempt to study the relationship between photodoping and fragility. In order to consolidate the existence of the relationship we must increase the number of case studies.

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Fig.1 Composition dependencies of the total amount of Ag photodissolved into amorphous Ge_xS_{1-x}, Y, the fragility determined from Raman scattering, I_{min}/I_{max}, and the fragility determined from viscosity measurements, F. The upper horizontal axis shows the average coordination number, $< r >$. The curves in the figure are guide to the eyes.

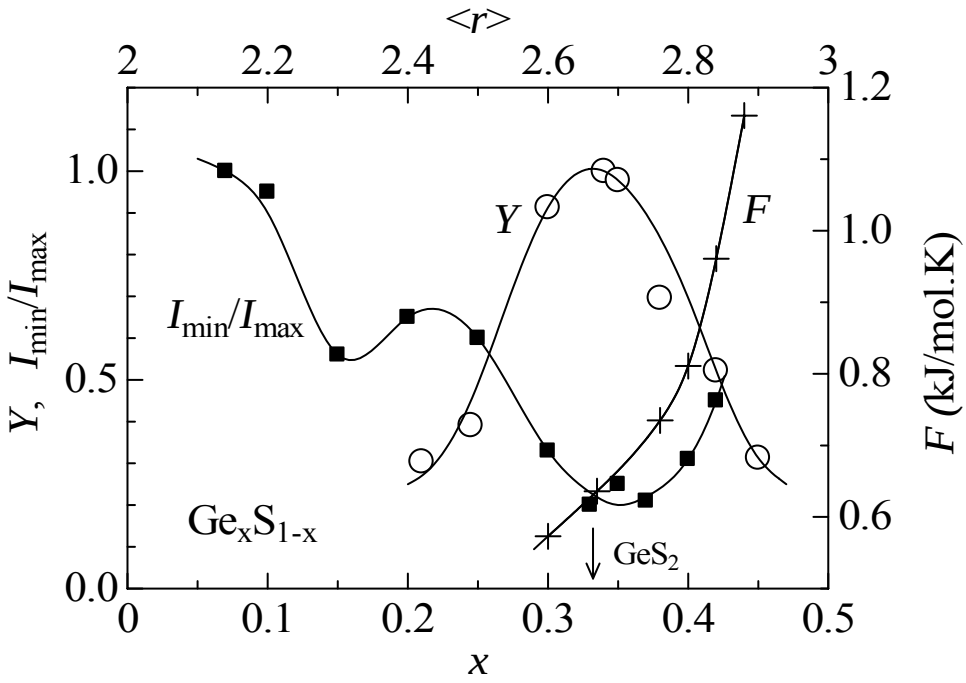

Fig.2 Temperature dependence of the viscosity of $Ge_{0.33}S_{0.67}$ and $Ge_{0.42}S_{0.58}$. The full and open circles are measured values [18] and the solid lines are theoretical ones given by Eq. 3.